INTRINSIC BIODEGRADATION STUDY WORK PLAN
HEWLETT-PACKARD
VOLUNTARY REMEDIAL ACTIONS
SAN GERMAN, PUERTO RICO

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1.0 INTRODUCTION



This Intrinsic Biodegradation Study Work Plan is submitted in support of the Hewlett-Packard Company (Hewlett-Packard) Voluntary Soil and Groundwater Remediation project at the Former Digital Equipment Corporation facility in San German, Puerto Rico (the "Site" – see Figures 1 and 2). The findings, opinions, conclusions, and recommendations presented in this report are subject to the Limitations provided in Appendix A.

The objective of the study is to evaluate whether Intrinsic Biodegradation would be a suitable remedial strategy for managing contaminant migration at this Site. The work plan summarizes the Site history and setting, and documents the effects of remedial efforts conducted by Hewlett-Packard and its predecessors on a voluntary basis between 1995 and the present. It describes current Site conditions, particularly as they pertain to the implementation of intrinsic biodegradation, and outlines a proposed monitoring program designed to evaluate the effectiveness of this remedial approach. Details regarding monitoring parameters, frequency of monitoring, data presentation, and reporting requirements have also been included in the work plan.

2.0 BACKGROUND AND SITE DESCRIPTION

2.1 SITE LOCATION AND HISTORY

The Site consists of approximately 18 acres, located on State Highway 362 in San German, Puerto Rico. It is located approximately 1,200 feet east of the Guanajibo River in a tributary drainage basin, and is bounded by a steep northeast to southeast trending ridge to the north and a smaller hill to the south. The topography generally slopes downward from the central portion of the Site towards the parking areas to the west and southeast with about 20 to 30 feet of relief.

The property is bounded to the north by undeveloped land, to the northwest and west by the Puerto Rico Electric and Power Authority (PREPA), to the south by State Road 362, and to the east by an industrial facility. The Site is owned by the Puerto Rico Industrial Development Company (PRIDCO), which leased the land to Digital Equipment Corporation (Digital) from July 1968 to 1992. Digital operated a printed wire board (PWB) and module assembly manufacturing facility at the Site, and in the mid-1970s, used trichloroethylene (TCE) in their Wave Solder Process as a degreaser and cleaning agent. Digital stopped using TCE in 1978, and terminated manufacturing operations at the Site in 1991. The facility was inactive until January 1993, when the Site was occupied by Circo Caribe. Circo Caribe manufactured PWBs at the Site until March 2001. In October 2001, PCB Horizon Technology Inc. leased the facility and began low-volume production of PWBs in November 2002. PCB Horizon Technology vacated the facility in 2005 and the facility remains vacant.



In preparation for the termination of Digital's lease of the facility, Digital completed two environmental investigations in 1992 and 1993. These investigations identified the presence of chlorinated ethenes (the presumed parent compound TCE and the assumed daughterdegradation product *cis*-1,2-dichloroethylene (1,2-DCE)) in the groundwater at the Site. The investigations concluded that TCE was likely to have been released from floor piping and wastewater trenches located at the facility production area. In response to these findings, Digital voluntarily implemented a remediation program.

Compaq purchased Digital in 1998, and assumed responsibility for the voluntary remediation efforts initiated by Digital. Subsequently, Hewlett-Packard merged with Compaq in 2002 and assumed responsibility for the operation of the remedial system.

2.2 GEOLOGIC AND HYDROGEOLOGIC SETTING

The Site geology generally consists of fill material overlying natural residual soils, which in turn overlie bedrock. The Site and vicinity were apparently filled and graded in the past. Areas likely to have been cut include the vicinity of topographic highs west of Building 1 and south of Building 5, whereas areas with the greatest fill include the western and central portions of the Site. The fill material ranges from stiff-to-hard clay and silt with up to 35 percent each sand and gravel, to medium-to-dense sand with up to 35 percent silt and clay and up to 35 percent gravel. The fill unit is absent in the south-central area of the Site and missing over most of the northern portion of the PREPA property. It is present at thicknesses of up to 23 feet across the central portions of the Site and the adjacent PREPA property, consistent with the presence of a generally east-west trending pre-development valley feature across the Site.

The natural residual soils consist of silt and clay soils underlain by saprolite formed by natural chemical weathering of the bedrock. The silt and clay layer appears discontinuous across the Site. The saprolite is typically denser than the clay and silt, has a greater gravel content, and has more evidence of primary rock textures and structures such as joints. It generally increases in density with depth, and has been differentiated from the bedrock by auger refusal.

The bedrock consists of altered mafic igneous rock, and was encountered at depths ranging from approximately 15 feet to greater than 50 feet below ground surface (bgs). The greatest depth of confirmed bedrock exists along the axis of the pre-development topographic valley in the central, northwest portion of the Site. Relatively shallow bedrock was observed in a soil boring near the southwest corner of Building 1, in the general vicinity of the pre-development topographic high.

Two groundwater systems are present at the Site; one appears to be perched within the shallow fill material with a water table ranging in depth from approximately 5 to 10 feet bgs, and the other is located in the saprolite and bedrock with a potentiometric surface ranging in depth from approximately 20 to 40 feet bgs. The depth of fill/alluvium ranges from approximately 10 to 30 feet bgs. Saprolite is located below the fill/alluvium layer, and its thickness ranges from approximately 10 to 40 feet. Bedrock is located below the



saprolite layer at approximately 20 to 60 feet bgs. A more detailed evaluation of the Site's hydrogeologic characteristics was presented in GZA's March 2003 Hydrogeologic Investigation Report, which assessed conditions across the Site with particular emphasis on the hydraulic connections between the fill, saprolite, and bedrock units.

The report indicated that, in the western part of the Site, a shallow perched aquifer water bearing zone in the western portion of the parking lot is located in silty clay fill and alluvial soils overlying the saprolite layer. The alluvium material, which has low gravel content, appears to act as an aquitard, limiting hydraulic conductivity connection between upper and lower layers and resulting in lower TCE concentrations in groundwater in the saprolite than in the fill. Phase I of the hydrogeologic investigation concluded that neither the fill nor the saprolite had been found to act as a significant migration pathway, and noted that under normal non-pumping conditions, flow of groundwater in the fill unit would be toward the west, with WB-1L representing downgradient conditions at the Site. The flow pattern has a semi-radial component affected by zones of more pervious backfill in the parking lot and infiltration of surface water from storm drains and the backfill material.

Phase II of the hydrogeologic investigation studied bedrock conditions in the central "A Street" area of the Site, and noted that the bedrock aquifer in the region between extraction wells W-1 and W-6 has extensive and widespread fracturing in at least the upper 40 feet of bedrock. The saprolite layer was observed to be extensively hydraulically connected to the bedrock aquifer in this region. It was further noted, based on observations during a rainfall event, that there was direct recharge to the fill above the saprolite, but this recharge was not observable in the saprolite or bedrock.

Phase III of the hydrogeologic investigation determined that the elevation of the bedrock appears to rise slightly from the center of the western parking lot to the western property boundary, and that the bedrock on the western property boundary is fractured but to a lesser extent than in the central part of the Site. Subsequently, Phase IV of the investigation, which included a 2-week period of non-pumping conditions at the Site, concluded that under non-pumping conditions, groundwater in the saprolite/bedrock unit would generally flow toward the pre-development valley in the center of the Site and then northwestward toward the Guanajibo River.

2.3 SOURCE AREAS

The historic TCE concentration data indicate two primary and one secondary general source areas. The highest concentration source area appears to be in the saprolite unit in the general area south of the Plant Chemical Storage Area (potentially also including TCE releases from former wastewater trenches under the production facility). The second primary source area, in the overburden fill unit, appears to be located just south of the Existing Hazardous Waste Storage Area, and may reflect previous use as a drum storage area. The secondary (and lower concentration) source area is represented by groundwater impacts in the fill and saprolite units in the vicinity of a stormwater catch

basin near the western property line, and appears to reflect historical seepage of unrelated release events through the bottom of the western boundary catch basin.



2.4 REMEDIAL GOALS

As stated in GZA's July 1995 RCRA Facility Investigation (RFI) Summary Report, the objectives of the voluntary remediation program at the Site were to:

- Contain and treat volatile organic compound (VOC)-containing groundwater; and
- Remediate VOC concentrations in the vadose zone soils to reduce impact to the groundwater.

To meet these goals, a Soil Vapor Extraction (SVE) system and a Groundwater Containment and Treatment System were installed at the Site. Details about the operation of these systems are provided in the following section.

2.5 REMEDIAL SYSTEMS

A soil vapor extraction (SVE) system was operated at the Site between October 1995 and November 2004. The system consisted of three SVE wells that extracted VOC vapors from the soil vadose zone in the front loading dock area of the Site, which was the only confirmed source area in soils for subsurface VOC contamination identified during investigations in the early 1990s. The SVE system was operated for over eight years, until three years of data indicated that the concentrations of VOCs in extracted vapor samples had achieved asymptotic levels. Based on these data, Hewlett-Packard received EQB's concurrence to deactivate and decommission the SVE system in a letter dated October 25, 2004. The SVE system was deactivated on November 11, 2004 and decommissioning was completed in February 2005.

Since 1995¹, VOC plume migration at the Site has been managed by a Groundwater Containment and Treatment System (GWCTS) currently consisting of the following components:

- Groundwater extraction wells (W-1, W-7, and W-8);
- Extraction well piping network;
- Groundwater treatment system (GWTS);
- Groundwater monitoring wells;
- A telemetry system; and
- An alarm auto-dialer.

¹ It is noted that prior to 1995, groundwater extraction was also generally being conducted by the on-site water production wells.



There are three wells currently incorporated into the groundwater extraction system: W-1, W-7 and W-8. The original function of these wells was to provide process water for facility operations when the facility was occupied and in production. However, there are currently no manufacturing operations at the Site, so there is no demand for process water. If water is needed in the future for operations, municipal water can be provided. Therefore, the extraction wells are no longer essential for facility operations.

From a remediation standpoint, the original function of these wells was to create and maintain a capture zone and deliver the extracted water to the GWTS for VOC removal. These wells are no longer required under the remediation plan presented below.

From a historic background perspective, the primary extraction wells used to create the capture zone during the recent past have been W-8 and W-7, because they had a greater influence on the downgradient groundwater capture zone than extraction well W-1. Of these two primary extraction wells, W-8 was the lead well given its proximity to the higher VOC-concentration areas at the Site. This well is located in the western parking lot, east of the basketball court, and is 350 feet deep. Extraction well W-7 is located in the southwestern corner of the western parking lot, toward which groundwater flowed prior to the installation of extraction well W-8. It was generally operated to extract impacted groundwater in this area, which is outside the capture zone of extraction well W-8. The total open depth of extraction well W-7 is 161 feet, based on field observations during the installation of a new pump and motor in the well during the week of June 8, 2009^2 .

Extraction well W-1 has historically been a backup well that was typically operated when: (1) a primary extraction well (W-7 or W-8) was not operational, or (2) the primary extraction wells could not provide sufficient water for facility process water use. Extraction well W-1 is 350-feet deep and is located in the northern area of the Site, in a shed north of Building 2 in the Plant Chemical Storage Area. It has currently replaced W-7 as one of the primary extraction wells at the Site.

The operation of the groundwater extraction wells is controlled by water level sensors in a 5,000-gallon equalization tank that is part of the GWTS. The GWTS is located in the northeastern portion of the Site. Groundwater treatment at the GWTS consists of filtration by basket strainers and sand filters for the removal of particulates and precipitated iron followed by carbon adsorption for the removal of VOCs, in particular TCE and 1,2-DCE which are the main contaminants of concern. Treated groundwater is preferentially routed to the facility for discharge directly to the sanitary sewer under Hewlett-Packard's Puerto Rico Aqueduct and Sewer Authority (PRASA) Authorization

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² It is believed that the original depth of extraction well W-7 was on the order of 350 feet, but this total depth has never been confirmed. The current, shallower open depth of 161 feet is believed to be the result of a borehole collapse below that point.

Discharge Authorization (AUA-E-06-313-018) if the facility does not require all the groundwater extracted³.



A telemetry system monitors the flow of groundwater from each extraction well and the flow of treated water from the GWTS. The GWTS auto-dialer alarm calls a local subcontractor if a GWTS system alarm is activated.

Influent and effluent samples are collected monthly and are tested for VOCs, including TCE and 1,2-DCE to evaluate the potential for breakthrough of the activated carbon, which is determined by increasing VOC concentrations in the effluent sample. Table 1 presents the results of influent and effluent sampling conducted during the last six months of 2009 in comparison to the results collected during the first two quarters of system operation. The liquid-phase carbon is replaced before breakthrough is reached. The spent activated carbon is shipped off-Site by a licensed waste management company for proper disposal or recycling.

2.6 GROUNDWATER MONITORING AND SAMPLING

Groundwater monitoring wells are gauged quarterly for groundwater elevation and sampled semi-annually for chemical concentrations to assess the groundwater capture zone of the GWTS. With the exception of well BR-308, which is a 6-inch diameter bedrock well, the monitoring wells consist of two-inch diameter wells that have been installed in the fill/alluvium, saprolite, and bedrock units. Each monitoring well is covered by a road box to protect it from vehicle traffic. A lockable well plug is installed in each monitoring well casing beneath the road box.

The groundwater level is measured quarterly at approximately 50 monitoring wells using a water level indicator, except for the groundwater elevations at six locations (GZ-507R, GZ-508R, GZ-509R, GZ-510R, GZ-512R, and GZ-513R) that are measured using pressure transducers. The monitoring wells at these locations have been closed; however, pressure transducers were installed prior to the well abandonment to provide ongoing information about groundwater elevations.

Groundwater samples are collected from approximately 25 monitoring wells on a semi-annual basis to monitor groundwater VOC concentrations, and the samples are submitted for laboratory analysis by US Environmental Protection Agency (USEPA) Method 8260C. The analytical results are certified by a Puerto Rico-certified chemist and are presented to PREQB in semi-annual reports.

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³ Manufacturing operations are not currently being conducted at the facility. Therefore, all of the treated groundwater is being discharged directly to the PRASA sewer.

2.7 PERFORMANCE OF EXISTING REMEDIAL STRATEGY



The primary objective of the existing groundwater extraction and treatment system was to control potential off-site migration of the plume, and also to reduce the dissolved VOC concentrations to the extent practical. Evaluation of Site conditions indicates that TCE concentrations greater than 100 µg/L continue to be detected only in the immediate vicinity of the source areas (in wells OW-304L/304R near the plant chemical storage area and in wells OW-305U and to a lesser extent GZ-502L at the hazardous waste storage area^[1]), and along A Street in the center of the Site (OW-101), suggesting that impacted groundwater has not significantly migrated away from these source areas. While one explanation for this limited migration is the impact of hydraulic control, it is also possibly due to naturally occurring processes that are biodegrading the chlorinated VOCs (cVOCs) in the subsurface and thus limiting the size of the dissolved plume.

The groundwater extraction and treatment system has been operated on a voluntary basis for 14 years. Over this period, influent concentrations to the system have remained relatively consistent and have averaged 0.025 mg/L TCE, resulting in removal of less than one liter of TCE per year.

Review of the current Site conditions indicates the present remedial approach is not a cost-effective or efficient means of removing VOCs from the subsurface. In addition, the effectiveness of natural biodegradation in controlling impacted groundwater cannot be evaluated while the extraction wells are in operation. In fact, operation of the groundwater extraction system may be limiting the effectiveness of intrinsic biodegradation, which is an anaerobic pathway at this Site, because the increased mass flux of oxygenated water through the respective formation has the effect of inhibiting reductive dechlorination.

As documented in the following sections of this work plan, there is evidence that intrinsic biodegradation of the cVOCs is occurring within the subsurface and may be successful at reducing cVOC concentrations in the groundwater. Therefore, GZA proposes to deactivate the groundwater extraction and treatment system during the period of time necessary to collect data and evaluate the effectiveness of intrinsic biodegradation as a remedial approach at this Site. At the conclusion of this evaluation, GZA will make a recommendation on whether the groundwater extraction and treatment system should be reactivated with the concurrence of the PREQB. A report will be submitted to the PREQB within three months of the completion of the Intrinsic Biodegradation evaluation. This will most likely be included as part of or as an appendix to a Semi-Annual Status Report.

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 $^{^{[1]}}$ TCE concentrations greater than 100 μ g/L are also detected on occasion in WB-1L, near the western perimeter of the Site.

3.0 EVALUATION OF INTRINSIC BIODEGRADATION AS A REMEDIAL APPROACH



An intrinsic biodegradation remedial approach refers to reliance on naturally occurring biological processes (within the context of a controlled and monitored site cleanup approach) to achieve site specific remedial objectives within a timeframe that is reasonable, compared to that of other remedial strategies. As defined by USEPA, the process depends on indigenous microflora to degrade contaminants without any remedial amendments (EPA, 2006, EPA/625/R-06/015). This approach is used *in situ* and takes advantage of naturally-occurring processes to degrade cVOCs, with careful monitoring to demonstrate the ongoing processes are protective of potential receptors.

Based on GZA's experience at several similar projects over the last decade, intrinsic biodegradation can be considered as an effective remedial approach for cVOCs in ground water when one or more of the following conditions are present at the Site.

- Intrinsic biodegradation is observed or strongly expected to be occurring.
- Potential receptors, if present, in the vicinity of the contamination will not be adversely impacted.
- VOCs are present that cannot be easily and cost-effectively removed and will require a long-term remedial effort.
- Alternative remedial technologies are not cost effective or are technically impractical.
- Alternative remedial technologies pose added risk by transferring or spreading contamination.
- Minimal disruption of facility operations or infrastructure is desired.

The following sections provide information regarding conditions at the San German Site with respect to the criteria listed above.

3.1 EVIDENCE OF ONGOING BIODEGRADATION

Biodegradation of chlorinated solvents occurs under anaerobic groundwater environments in the presence of microbial species capable of degrading these compounds through respiration to various daughterdegradation compounds. Biologically reductive dehalogenation (BRD) typically results in the sequential breakdown of the chlorinated parent compound TCE to its daughterdegradation compound 1,2-DCE, which in turn is dechlorinated to yield vinyl chloride, which in turn is dechlorinated to yield ethene. The rate of biodegradation is controlled by several factors related to the availability of required elements (e.g., an organic carbon "food" source), nutrients, and growth factors necessary for the viability of the microbial population.

Intrinsic biodegradation can be evaluated using a "line of evidence" approach, including the following:

• Primary Line of Evidence - Documentation of loss of contaminants through



- reviewing historical trends in contaminant concentration and distribution in conjunction with Site geology and hydrogeology, to show that reduction in total mass of contaminants is occurring.
- Secondary Line of Evidence Evaluation of the change in concentration and distribution of geochemical and biological indicator parameters that have been correlated to biodegradation pathways.

At this Site, evaluation of the groundwater TCE concentrations over time indicates a generally decreasing temporal trend (primary line of evidence), particularly at the source areas of the Site, where concentrations are currently less than half of historical high concentrations. Appendix B presents graphs of the historical concentrations of TCE, 1,2-DCE, and vinyl chloride (VC) over time for eighteen monitoring wells that have been routinely sampled. In general, the concentrations of TCE at the wells have exhibited a downward temporal trend. For example, TCE concentrations at well cluster OW-304, located near a primary source area, have decreased from greater than 70,000 μ g/L to 6,300 μ g/L4 in well OW-304L (screened in saprolite) and from greater than 15,000 μ g/L to 1,000 μ g/L in well OW-304R (screened in bedrock).

In addition, the data confirm increasing concentrations of 1,2-DCE relative to TCE, indicating that the TCE released by former operations is being degraded to its daughterdegradation by-product 1,2-DCE and suggesting that intrinsic biodegradation may be a viable option for remediation of the residual groundwater contamination. Given that one mole of TCE yields one mole of 1,2-DCE via a reductive dechlorination pathway, mass per volume measurements of each parameter are biased by the mass difference between both chemical compounds (i.e., while one mole of TCE yields one mole of 1,2-DCE, one gram of TCE yields less than one gram of 1,2-DCE) due to the replacement of the heavier chlorine atom with a lighter hydrogen atom. To normalize the data for the purpose of evaluating the TCE to 1,2-DCE transformation path, GZA converted these compounds from mass per volume (concentrations) to their molar equivalencies. Molarity trend analyses (Appendix C) more clearly illustrate a shift toward 1,2-DCE dominance at the Site. In the absence of a release of both TCE and 1,2-DCE, the relationship between TCE and 1,2-DCE is that of parent to daughter degradation compound, where the daughterdegradation compound represents a dechlorination product of the parent compound. At this Site, data from most wells show a generally higher concentration of 1,2-DCE than of TCE and some (GZ-504R, GZ-502L, and OW-404L) with a recent trend demonstrating an increasing temporal dominance of 1,2-DCE over TCE. Four wells (OW-101, GZ-506R, OW-304R, and OW-304L) show a higher TCE concentration over 1,2-DCE. However, of the four wells, three show the TCE concentration approaching the 1,2-DCE concentration. The one exception, GZ-506R, is located between a historic source area and the extraction wells; thus the recent change in the primary extraction wells could explain why this particular well exhibits an increase in TCE.

Given the above observations it can be concluded that the most likely explanation for the 1,2-DCE dominance at the Site is that biodegradation is occurring via a reductive

⁴ *i.e.*, the lowest TCE concentration detected at this well for more than a decade.

dechlorination pathway, converting TCE to 1,2-DCE (because there has been no known release of 1,2-DCE on Site).



3.2 POTENTIAL RECEPTORS

In evaluating intrinsic biodegradation, one of the primary considerations is the potential effects on potential receptors at and around the release area. At this Site, there are no current human receptors on the property, which has been unoccupied since 2005. Access to casual human visits (i.e., trespassers) is limited by a fence around the property and security measures provided by PRIDCO. Extended access by construction or utility workers, while possible, is not anticipated in the next several years. Changes in Site use are not anticipated during the period of evaluation of the feasibility of implementing a biodegradation remedy. If such changes do occur during the evaluation, an assessment of the potential risks to such receptors will be performed at that time based on the nature of the changed use. Currently, the nearest potential human receptors in the vicinity of the Site include workers at the facilities located east and west of the Site, and residents located to the south of the Site. Since the cVOCs at this Site are present in groundwater at depths of greater than 5 feet below grade, direct contact is not considered a complete exposure pathway. Instead, the risk to potential receptors would be inhalation risks associated with vapor intrusion into occupied buildings. In order to evaluate these risks, the maximum dissolved groundwater concentrations in the perimeter wells at the Site were compared to numerical values for TCE (5 μg/L) and cis-1,2-DCE (210 μg/L) listed in Table 2b of EPA's November 2002 OSWER Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (EPA530-D-02-004). Per the guidance document, these numerical values represent "conservative 'generic' attenuation factors that reflect generally reasonable worst-case conditions for a first-pass screening of groundwater [...]."

Along the western perimeter of the Site, the screening evaluation was based primarily on data from wells GZ-504U, WB-1U, OW-404U, WB-2U, WB-3L, WB-4L, and GZ-515U, which represent groundwater conditions in the uppermost aquifer at each of these locations (i.e. in the case of the GZ-504 cluster, data from GZ-504U was used to represent the uppermost fill aquifer; in the case of WB-3L, the data was used even though the well is screened in saprolite because it is the most shallow groundwater data available for this location). The comparison indicates that with the exception of WB-2U, where the maximum TCE concentration of 8 μ g/L slightly exceeds the screening value of 5 μ g/L, the dissolved concentrations in the wells listed above were below the screening values for TCE and cis-1,2-DCE. It should be noted that the 8 μ g/L concentration reported for WB-2U may be anomalous, since the well was sampled on 14 occasions, and TCE concentrations on the 13 other occasions were consistently below the detection limit of 1 μ g/L. Therefore, based on this screening evaluation, the potential inhalation risk to receptors west of the Site does not represent an unacceptable risk.

Along the eastern perimeter of the Site, the maximum dissolved TCE and cis-1,2-DCE concentrations from perimeter wells OW-301, OW-407, and OW-1 and W-5 were found

to be below the <u>US</u>EPA screening values, indicating that the potential inhalation risk to receptors east of the Site does not represent an unacceptable risk.



Data from the southern boundary of the Site are more limited, and less conclusive. Historic maximum TCE concentrations along the south-eastern portion of the southern boundary, represented by monitoring wells OW-302 and OW-303A, which are screened in highly weathered rock, exceed the screening value of 5 μ g/L. However, there were only two data points for OW-302, and review of the OW-303A data indicate that the average TCE concentration over 19 sampling episodes was 4 μ g/L, below the screening value of 5 μ g/L. Based on these data, inhalation risks associated with groundwater in the south-eastern part of the Site does not represent an unacceptable risk.

Shallow groundwater concentrations along the southern boundary west of "A" Street are represented by monitoring wells OW-405, GZ-516U, and GZ-515U. Of these, the TCE concentration in well OW-405 was 60 µg/L in 2003, but insufficient water was present in the well to confirm this result during 8 subsequent sampling events; TCE and cis-1,2-DCE concentrations in the latter two wells have been consistently below the EPA screening values. Additionally, it is anticipated that under non-pumping conditions groundwater flow will be towards the center of the site and northwestward toward the Guanajibo River. Based on the data from GZ-516U and GZ-515U the potential inhalation risk represented by groundwater concentrations along the southern boundary of the Site does not represent an unacceptable risk. As part of the proposed biodegradation monitoring program additional data is scheduled to be collected from monitoring wells GZ-515U and OW-405 and the potential for risk associated with vapor intrusion will be further evaluated.

GZA's 1995 risk characterization evaluated the risks associated with ingestion and dermal contact with groundwater from private water supply wells. It concluded that there were no registered private wells in the vicinity of the Site. In January 2010, GZA conducted a review of PRASA's records and concluded that there remain to be no registered private water supply wells used for drinking water in the vicinity of the Site. Groundwater elevations and perimeter well concentrations along the southern and western Site boundaries will be closely monitored during the intrinsic biodegradation study as described later in this document, and changes of groundwater flow direction or increases in perimeter concentrations will be evaluated to assess their potential impact on nearby receptors. If data indicate that groundwater is migrating off-site and may have an impact on potential off-site receptors, GZA will propose additional responses as described in Section 4.7 (Contingency Plan). Also, the potential for off-site impacts will be taken into consideration when evaluating whether intrinsic biodegradation can be successfully implemented as a long-term remedial approach.

The primary <u>surface water body environmental receptor</u> in the vicinity of the Site is the Guanajibo River, located <u>downgradient and</u> approximately 1/3 mile west and ½ mile south of the property. As in the case of human receptors <u>or targets</u>, data from the perimeter monitoring wells will be evaluated during the intrinsic biodegradation study,

and data suggesting increased off-Site migration will be incorporated into the decision process regarding the suitability of intrinsic biodegradation as a remedial alternative.



3.3 ALTERNATIVE REMEDIAL TECHNOLOGIES

Remedial technologies, including soil vapor extraction to address vadose zone contamination and groundwater pumping and treatment to address groundwater VOC concentrations, have been implemented at the Site. The groundwater extraction and treatment system has been operational for over 14 years, and the data demonstrate that the residual source material is not being effectively removed using this technology. Therefore, we are recommending that the alternative technology of intrinsic bioremediation be evaluated. It should be noted that this work plan also includes a contingency to consider other alternative technologies, such as in-situ chemical oxidation or enhanced bioremediation, if the intrinsic biodegradation study indicates the need for additional remediation.

3.4 DISRUPTION TO SITE OPERATIONS

Disruption to Site operations is not a consideration at this Site because the facility is no longer in operation.

3.5 APPLICABILITY OF INTRINSIC BIODEGRADATION

The Site meets three of the key conditions for implementation of intrinsic biodegradation: 1) there is evidence that ongoing bioremediation is occurring at the Site; 2) use of biodegradation is unlikely to pose a significantly increased risk to receptors; and 3) there are still contaminants in the groundwater after many years of treatment. It is GZA's opinion and the data support that mass removal of VOCs via the GWCTS is de minimis. Therefore, the more cost efficient remedial option of intrinsic bioremediation, which is expected to be at least as effective, should be tried. In fact, it is not only clear that intrinsic bioremediation is currently removing VOC mass from the Site, but it is likely to become more effective once the current operation of the groundwater extraction system is This is because intrinsic biodegradation is an anaerobic pathway on Site deactivated. and the increased mass flux of oxygenated water through the formation due to the pumping has the effect of inhibiting reductive dechlorination; as such, intrinsic biodegradation should be enhanced relative to its current level of effectiveness if the groundwater extraction system is deactivated. Therefore, GZA proposes to deactivate the existing system during the implementation of the intrinsic biodegradation study as described in the next section of this report.

4.0 DESCRIPTION OF PROPOSED STUDY



4.1 REMEDIAL ACTION OBJECTIVES

The objective of the proposed study is to evaluate whether, in the absence of any additional remedial technologies, intrinsic biodegradation of the residual cVOCs in groundwater can continue to reduce dissolved concentrations while posing no additional risk to human or environmental receptors. To this end, the study proposes to deactivate the GWTS including all extraction wells at the Site and monitor groundwater elevations and VOC concentrations as described below. It should be noted that the GWTS will remain at the site and be ready for reactivation if the need arises and data collected indicate that reactivation is warranted.

4.2 MONITORING OBJECTIVES

The principal objectives of groundwater monitoring are three-fold: (i) to evaluate whether dissolved concentrations at the Site continue to decline; (ii) to monitor the relative concentrations of TCE and its daughterdegradation compounds, as well as other known biologically sensitive parameters described in Section 4.4, in order to confirm biodegradation is occurring and the respective degradation pathway; and (iii) to monitor conditions at perimeter wells to evaluate the potential for off-Site migration of impacted groundwater.

4.3 MONITORING OF GROUNDWATER ELEVATIONS

Groundwater elevations across the Site under non-pumping conditions will be monitored throughout the study to assess the direction of groundwater flow in each of the hydrogeologic units. A groundwater level indicator will be used to measure the depth to groundwater in each of the on-Site monitoring and extraction wells following shutdown of the extraction wells. Groundwater levels from the adjacent property north of the Site will be collected via the pressure transducers installed at locations GZ-507R, GZ-508R, GZ-509R, GZ-510R, GZ-512R, and GZ-513R. Groundwater level measurements will be performed weekly for the first month, monthly for six months, and quarterly thereafter. The frequency of gauging may vary depending on groundwater rebound response and other factors.

4.4 SAMPLING PARAMETERS

Based on the constituents of concern at the Site, a key parameter to be measured during the study will be cVOC concentrations in groundwater monitoring wells across the Site. These data will be used to evaluate whether concentrations in each of the geologic units continue to decrease over time, and to monitor any potential off-Site migration.



Other chemical indicators representative of ongoing biodegradation will also be measured during the study. The process of biodegradation for cVOCs is largely based upon microbial respiration, during which cVOCs serve as electron acceptors to receive the electrons released during the metabolism of organic carbon, the electron donors. During this process (dehalorespiration), microbes gain energy from the consumption (oxidation) of electron donors coupled to the utilization (reduction) of electron acceptors. Dissolved oxygen (DO), which can serve as a terminal electron acceptor (TEA) and limit cVOC dechlorination by competing with the cVOCs for hydrogen and volatile fatty acids (VFAs)⁵, will be measured during each sampling event. In general, DO measurements of less than 0.5 ppm suggest that anaerobic conditions conducive for cVOC dechlorination may exist. Under anaerobic conditions (i.e., in the absence of DO), electron acceptors such as nitrate, ferric iron, and sulfate are respectively utilized for nitrate reduction, ferrogenic, and sulfate reduction. Each of these pathways competes with cVOCs for hydrogen and VFAs, so additional groundwater samples will be collected for analysis of nitrate, ferrous (iron II), and sulfate. Other parameters that will be measured include the total organic carbon (TOC) concentration, which is a primary parameter that drives cVOC dechlorination by providing electron donor to native soil bacteria; the oxygenreduction potential (ORP)6, which serves as an indicator of the Redox conditions that control cVOC dechlorination; pH, which acts as a general indicator of conditions conducive for natural biota (dechlorinating microorganisms can be particularly sensitive to low pH conditions); and methane, which is an indicator of anaerobic, chemically reducing conditions that can support cVOC dechlorination.

Samples will also be analyzed for chloride, which is a dechlorination product of cVOCs, and for ethanes and ethenes, the end products of cVOC reductive dechlorination, whose presence would demonstrate that the reaction is proceeding to completion.

4.5 SAMPLING FREQUENCY

Groundwater samples from monitoring wells screened in the alluvium/fill, saprolite, and bedrock units at the Site will be analyzed for the suite of geochemical parameters described in the previous section to evaluate the effectiveness of the intrinsic biodegradation process.

Prior to initiation of the intrinsic biodegradation study, the 47 monitoring wells listed on Table 2–1 will be gauged and sampled to establish baseline conditions at the Site. Subsequently, as documented on Table 32, 30 of the wells will be sampled on a semi-annual basis, and the remaining 17 wells (designated in bold font on Table 32) will be sampled biennially (once every other year), unless TCE concentrations in proximal wells

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⁵ Note that hydrogen and VFAs are the "food" that drive reductive dechlorination. Without these electron donors, dechlorination cannot proceed via a dehalorespiration pathway.

⁶ Theoretically, aerobic degradative activity occurs at a highly positive redox potential, while anaerobic microbial processes such as methanogenesis and sulfate reduction will occur at strongly negative redox potentials; however interpretation of redox potential field data in terms of microbial activity can be extremely challenging, as these measurements are due to complex interactions between chemical species present in the groundwater and microbial byproducts.



begin to increase, in which case they would be sampled semi-annually. Based on their location and the current trends in cVOC concentrations, wells will be measured for either a limited sub-set of parameters (35 wells) or for a complete set of parameters (12 wells) as documented on Table 32. Table 2 provides the rationale for the selection of semi-annual versus biennial sampling and limited versus complete parameters for each well. It also describes the difference between the limited set of parameters and the complete set.

Further details regarding sample collection methods, sample preservation and handling, chain-of-custody procedures, analytical procedures, and field and laboratory quality assurance/quality control will be provided in a site-specific Quality Assurance Project Plan (QAPP) that is included as Appendix D of this work plan. The QAPP, which documents the manner in which quality assurance and quality control activities will be implemented throughout the study, is composed of the following elements:

- Description of project tasks, data quality objectives, and management,
- Description of data acquisition and management,
- Description of assessments, responses, and oversight, and
- Description of data validation, verification, and usability.

4.6 DATA EVALUATION

The data collected from the monitoring wells across the Site will be evaluated throughout the study period to assess the effectiveness of intrinsic biodegradation for remediating cVOC in groundwater at the Site. In addition, the groundwater monitoring data will be closely reviewed to evaluate groundwater flow patterns in the absence of on-Site pumping.

4.6.1 Geochemical Evaluation

The primary indicator of ongoing biodegradation at the Site is anticipated to be a decrease in dissolved TCE concentrations, with a concurrent increase in 1,2-DCE and other daughterdegradation products relative to TCE concentrations in groundwater. Therefore, the dissolved TCE, 1,2-DCE, and VC concentrations will be plotted with historic data to evaluate whether the general temporal decrease seen in the current data continues over time. The data will also be used to evaluate whether the 1,2-DCE dominance of the Site continues, indicating continued breakdown of TCE into its daughterdegradation products.

If the results of the primary lines of evidence are not conclusive, then additional geochemical data will be evaluated to assess whether secondary lines of evidence support ongoing intrinsic biodegradation. For example, decreasing ORP, DO, nitrate, ferric iron

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⁷ Additionally, monitoring wells that are sampled semi-annually that indicate an increase in cVOC concentration may be sampled at intervals more frequently than semi-annually.

or sulfate values, or increasing ethane, ethene or chloride concentrations, would generally be indicative of conditions suitable for cVOC reductive dechlorination at the Site.



4.6.2 Groundwater Elevations

Groundwater level monitoring data collected from the wells in each geologic zone will be evaluated to assess the change in flow patterns at the Site following shutdown of the groundwater treatment system. Hydrographs will be created to chart groundwater elevations until hydraulic conditions stabilize, following which the groundwater elevation data will be contoured on a semi-annual basis to assess flow direction in the fill, saprolite, and bedrock zones at the Site. Rebound of groundwater levels to natural conditions is anticipated to be slow; however, if the data suggest that flow patterns are drastically different from those anticipated, the frequency of groundwater level monitoring will be increased in order to provide a more complete understanding of groundwater flow direction with respect to source areas and potential receptors. Additional measures to address changes in flow patterns are discussed in the contingency section below.

4.7 CONTINGENCY PLAN

The objective of the contingency plan is to identify certain conditions that would likely warrant action based on the ongoing review of the data being collected. The groundwater levels and static contaminant concentrations may take time to reach equilibrium. Additionally, it may take several rounds of data collection after that time to gain clarity and a reasonable level of certainty that equilibrium was established, and as a result the establishment of temporal and/or spatial concentration trends will be a protracted process. However, if an unfavorable condition is observed and confirmed, corrective actions will be implemented. Unfavorable conditions that would be of particular concern include confirmed trends demonstrating significantly increasing concentration of TCE in groundwater migrating off-site, reversal of daughterdegradation product dominant concentrations, absence of supporting data regarding intrinsic biodegradation activity from secondary lines of evidence and/or evidence of plume advancement. If such conditions are suspected and confirmed, additional remedial response actions will be considered, including enhanced biodegradation or in-situ chemical oxidation for localized areas, activation of select groundwater extraction wells associated with the GWCTS, and/or other remedial approaches that are deemed appropriate for the given condition. Similarly, if groundwater contouring indicates that flow patterns are significantly different than anticipated, additional monitoring wells may be installed downgradient of Site in the direction of groundwater flow.

A section of each status report will be dedicated to an evaluation of areas of concern and/or potential conditions (trends) being observed along with an explanation of actions or potential actions to be implemented.

4.8 REPORTING



Status reports will be prepared on a semi-annual basis for submission to PREQB with a copy to USEPA Region 2. As is currently being performed, each status report will cover a six-month period (January through June and July through December). The Semi-Annual Progress Reports will contain the following information:

- Description of the type and frequency of monitoring activities conducted;
- Summary of data obtained during the reporting period, including groundwater elevation data, analytical data reports, and tables and charts of relevant groundwater parameters;
- Status of response operations and description of significant modifications;
- Description of issues which may affect the performance of the remedial strategy and corrective actions to be conducted; and
- Planned activities for next reporting period.

5.0 REFERENCES

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